SINTERABILITY OF LOW-MELTING ILLITE-BEARING CLAYS

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A sintered ceramic materials with water absorption below 6% is obtained on the basis of low-melting illite-bearing clays with a finely dispersed glass additive. The dependence of the properties of sintered ceramic mixtures on the quantitative ratio of raw material to the finely disperse additive is established. The process of crystallization of minerals in firing ceramic mixtures is investigated.

The process of firing is one of the most significant stages in the production of ceramic articles. The probability of deformation of products is the highest in firing and especially high in using materials with a narrow sintering interval (approximately 50°C).

It is possible to control the sintering process by using mineral additives that increase the amount of the liquid phase in firing. It was earlier shown [1] that synthetic pseudo-wollastonite and nepheline sienite can be used as additives for a ceramic mixture consisting of three illite-bearing clays different in their chemical and granulometric compositions. Completely sintered ceramics was obtained with a 15% additive of synthesized pseudowollastonite or nepheline sienite, and the sintering process took place in a temperature interval of 1060 – 1150°C (the sintering interval thus extended from 60 to 90°C). A cullet additive as well has an effect on the sintering process [2]. It is established that the quantity of additive varies from 5 to 15% depending on the materials used.

The production of sheet glass generates finely dispersed glass waste with a high specific surface area. This waste can be used as additive to obtain sintered ceramics.

The present study investigated a system consisting of natural low-melting aluminosilicates (illite clays) and finely dispersed glass waste (hereafter called "finely dispersed cullet additive") for the purpose of identifying the dependence of the properties of sintered ceramic mixtures (heating shrinkage, water absorption, melting point) on the ratio of material to the cullet additive, as well as the process of crystallization of minerals in ceramic mixture firing.

Two varieties of illite-bearing clays were used: a Devonian clay (clay A) and a Quaternary clay (clay B). The chemical composition of the clays and the finely dispersed glass additive (specific surface area 7830 cm^2/g) is listed in Table 1. These are clays with a small sintering interval (30 – 75°C). Clay A is contaminated with large carbonate inclusions and belongs to acid and semiacid clays. X-ray phase analysis indicates that the crystalline structure of clays A and B includes hydromica, chlorites, kaolin, quartz, feldspars, dolomite, calcite, and hematite.

Dilatometric analysis was performed using a DKV dilatometer with a corundum tube within a temperature interval of 20 – 1000°C, the rate of temperature rise being equal to 4 K/min. Shrinkage variations were measured with an indicator (scale factor 0.01 mm) each 10 min. Structural variations of ceramic mixtures in firing were investigated using a DRON-2 x-ray diffractometer. Water absorption was determined by exposing sample in water for 48 h at a temperature of 20 ± 5°C. The melting point of ceramic mixtures was

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TABLE 1

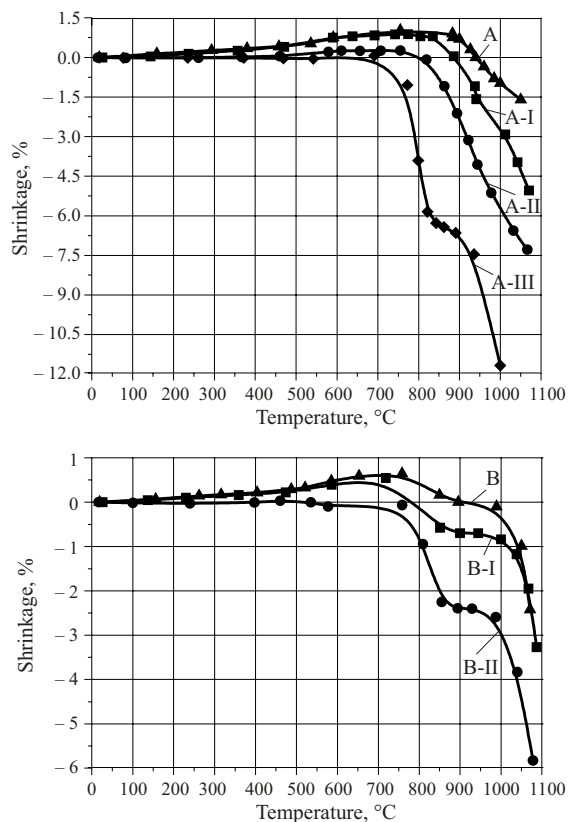| Material	Mass content, %							
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	calcination loss
Clay:								
A	66.33	15.64	1.11	1.80	5.90	2.54	0.40	4.86
B	68.70	18.43	1.80	2.72	6.42	1.63	–	6.85
Finely dispersed glass additive	72.20	1.48	7.80	3.65	0.08	13.70		–

Fig. 1. Dilatometric curves of samples.

measured using a high-temperature MNO-2 microscope (temperature rise rate 4 K/min).

The compositions of molding mixtures are listed in Table 2. Cylindrical samples (33×42 mm) were molded from these mixtures to study sintering. Dilatometric analysis was performed on samples of size 8×60 mm. The clays were dried to a constant mass at a temperature of $110 \pm 5°C$, crushed on a jaw crusher, and sifted through a No. 1 sieve. Mixtures prepared for molding were aged for 2 days. The finely disperse glass additive was dried to a constant mass at the same temperature conditions as clay and sifted through the same sieve.

TABLE 2

| Sample* | Content, % | |
	clay	finely dispersed glass additive
A-I	90	10
A-II	80	20
A-III	50	50
B-I	90	10
B-II	80	20
B-III	50	50

* Samples A-I, A-II, and A-III contain clay A, samples B-I, B-II, and B-III contain clay B.

To determine the effect of the quantity of the disperse cullet additive on the temperature of the beginning of the liquid phase formation (and, accordingly, on the start of sintering of ceramic mixture), dilatometric measurements were carried out (Fig. 1). It was found that the finely dispersed cullet additive effectively increases the shrinkage of samples A-II and A-III, and their deformation regularly grows with an increasing additive content. At 1000°C the deformation of sample A-I is similar to the deformation of sample A, whereas sample A-III at this temperature is deformed to a higher extent: its deformation is 12%.

Expansion of molding mixtures based on clay A is due to thermal expansion of solid materials, to dehydration and decarbonizing processes, and to the emergence of amorphous phases as a consequence of reactions of calcium oxide with aluminosilicate materials. Shrinkage is caused by crystallization of new phases and melting of the finely dispersed glass additive. As the amount of the additive increases, the shrinkage starting temperature (and, accordingly, the starting temperature of the liquid phase formation) is shifted to a lower temperature zone. Thus, the start of shrinkage in sample A-I is registered at 800°C, whereas the start of shrinkage of samples A-II and A-III is registered at 750 and 700°C, respectively. The finely dispersed additive levels the thermal expansion during dehydration of argillaceous materials and the formation of amorphous phases, thus decreasing the TCLE. It is established that the deformation start temperature of sample A-II correlates with the temperature of crystallization of hematite Fe_2O_3 (Figs. 1 and 2a). Evidently the shift of the temperature of the liquid phase formation to a lower temperature zone is possible when the finely dispersed glass additive is used in an amount over 10%.

Dilatometric studies of model molding mixtures based on clay B (Fig. 1) established that shrinkage of samples occurs in two stages. The first stage starts at a temperature of 700°C and the second one at 900°C. The start of shrinkage at 700°C, as well as a sharp increase in the quartz peak intensity (Figs. 1 and 2b), indicate the start of melting of the finely dispersed glass additive and the reaction of quartz with Na^+ ions contained in the glass additive. Shrinkage of samples is facilitated as well by decomposition of dolomite; however, free CaO has not been identified, which points to calcium oxide reacting with the x-ray-amorphous aluminosilicates that make up part of clay B.

Dilatometric studies of sample B-I and B-II indicated that when the glass additive is used, there is a clearly expressed transition from the first stage of shrinkage to the second one (Fig. 1). The glass additive has an effect on the shrinkage of molding mixtures based on clay B when introduced in an amount over 10%. The deformations of samples based on clay B and molding mixture B-I are similar and at 1050°C virtually coincide. The effect of the glass additive in an amount of 20% is even more significant. At 1070°C the shrinkage of sample B-II was around 6%, whereas that of sample B-I was 2.5% and that of clay B was 2.0%. At the same time, no shift in the shrinkage start temperature (ac-
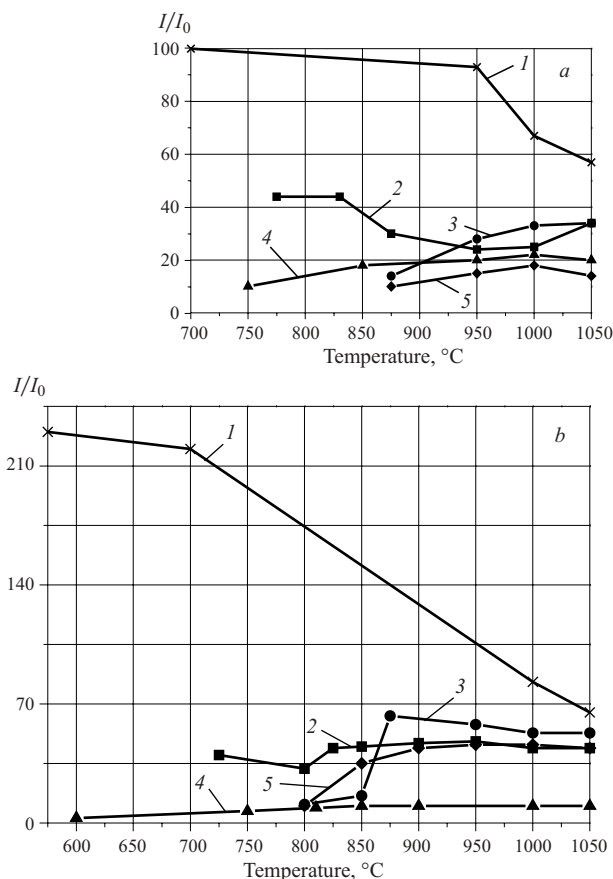
Fig. 2. Sequence of crystallization of new phases in sintering of ceramic mixtures A-II (*a*) and B-II (*b*): *1*) quartz, *2*) albite, *3*) cristobalite; *4*) hematite; *5*) diopside.

Fig. 3. Dependence of water absorption of samples on firing temperature.

cordingly, the temperature of liquid phase formation) to a lower-temperature zone was registered. Consequently, the start of the liquid phase formation does not depend on the quantity of the finely dispersed glass additive introduced.

The water absorption of molding mixtures based on clays A and B is represented in Fig. 3. The finely dispersed glass additive in an amount of 10% has no effect on the sintering of samples A-I and B-I and acts as a grog component. When the content of the glass additive grows to 20%, its fluxing ability is manifested to a higher degree. A level of water absorption below 6% in sample A-II is reached at a temperature of 900°C, and the sintering interval of ceramic mixture expands from 75 to 200°C compared to clay A. Water absorption of sample B-II below 6% is achieved at 1000°C and the sintering interval grows from 50 to 100°C.

X-ray phase analysis was used to study the process of crystallization in sintering ceramic mixtures A-II and B-II (Fig. 2). It was established that hematite Fe_2O_3 crystallizes in mixture A-II at 750°C. Recrystallization of potassium-sodium feldspars occurs at a temperature of 850°C. The x-ray curves exhibit a decrease in intensity in peaks 3.25 Å and a subsequent increase in line 3.19 Å. It follows that the minerals that crystallized are of the plagioclase class (albite
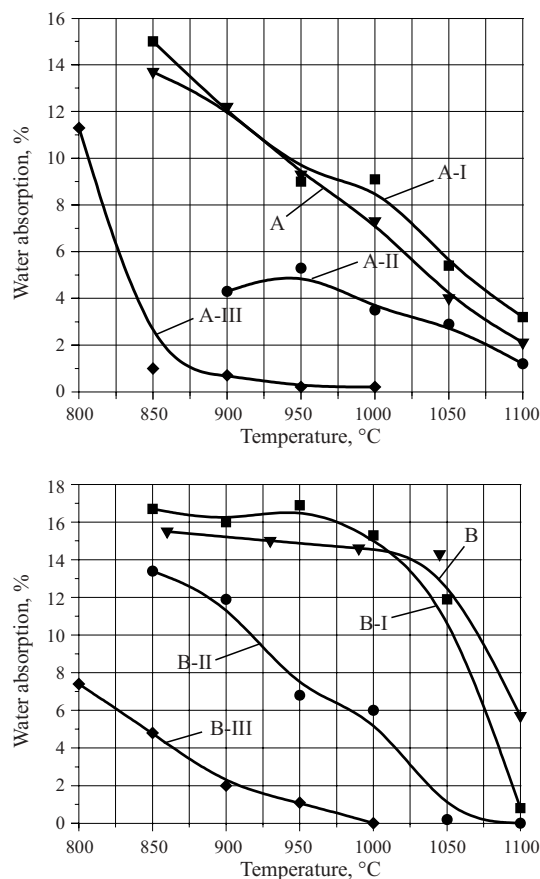
$NaSi_3AlO_8$). Analysis of the chemical composition of clay A and the finely disperse additive indicates that the additive contains more sodium, calcium, and magnesium ions than clay A does (Table 1). Therefore, a concentration gradient of the specified ions is formed in a ceramic mixture. As a result, Na^+ ions contained in the glass additive diffuse. Since the diffusion coefficient of Na^+ ions is higher than that of Ca^{2+} and Mg^{2+} ions, Ca^{2+}, Mg^{2+}, and Si^{4+} ions become concentrated in the glass additive, which facilitates the crystallization of diopside $CaMgSi_2O_6$ and cristobalite at a temperature of 875°C.

X-ray studies of mixture B-II established that the crystallization of cristobalite and diopside takes place at 800°C, and hematite is formed at 600°C. The intensity of the cristobalite peak sharply grows within a temperature interval of 850 – 875°C. This is due to the fact that quartz is transformed at 870°C into an intermediate stage of tridimite [3]. Apparently, the rate of crystallization increases in the course of formation of the intermediate phase, and tridimite changes over to cristobalite in the presence of Na^+ ions already at 875°C. The narrow temperature interval of the phase transformation of tridimite into cristobalite and the sharp increase in the cristobalite peak intensity at 875°C point to the high intensity of phase transformations.
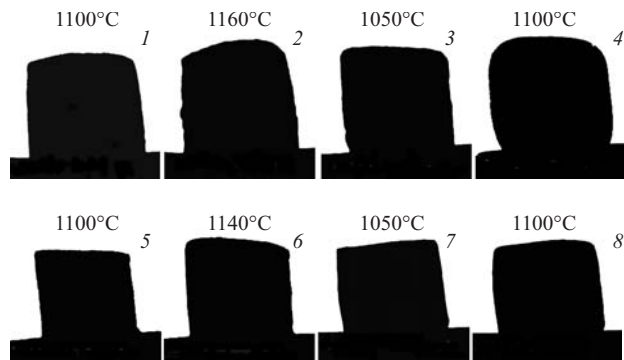
Fig. 4. The effect of finely dispersed glass additive on the melting point of ceramic mixtures A-II (*1*, *2*), A-III (*3*, *4*), B-II (*5*, *6*), and B-III (*7*, *8*).

The results of studying the effect of the finely dispersed glass additive on the melting point of model molding mixtures using a high-temperature microscope are presented in Fig. 4. It is established that the outer contour line of sample A-II does not change within the temperature interval from 20 to 1100°C but changes at 1150°C. The melting process starts at 1160°C. The start of melting is indicated by a sharp expansion of the sample and by rounding of the upper line of its outer contour. The melting start temperature has shifted to a lower temperature zone. The outer contour line of sample A-III does not change in the temperature interval from 20 to 1000°C. At 1050°C a sharp expansion of the sample is recorded, and the melting starting point is 1100°C. Analysis of the results showed that the melting process changes depending on the quantity of the glass additive. Thus, there are local contour variation in sample A-II at the beginning of the melting process, whereas sample A-III exhibits variations over the whole contour perimeter.

In firing sample B-II in a temperature range from 20 to 1100°C, no evident indication of its shape have been observed, and the melting start temperature is 1140°C. The shape of sample B-III does not change in the temperature interval from 20 to 1050°C, whereas its melting start temperature is 40°C lower than that of sample B-II.

Thus, sintered ceramic materials with water absorption below 6% can be obtained on the basis of low-melting illite-bearing clays with a finely dispersed glass additive. In using the glass additive, the temperature interval of sintering of a ceramic mixture based on clay A expands from 75 to 200°C, and the interval for the mixture based on clay B grows from 50 to 100°C. Minerals of quartz, diopside, hematite, and cristobalite crystallize during the diffusion of Na^+, Ca^{2+}, and Mg^{2+} ions in sintering of ceramic mixtures. Depending on the clay used, the temperature of crystallization of hematite varies. Hematite emerges at 750°C in sample A-II and at 600°C in sample B-II.

The possibility of lowering the melting point for samples based on clay A (from 1160 to 1100°C) and clay B (from 1140 to 1100°C) has been established. To do this, the amount of finely dispersed glass additive should be increased from 20 to 50%.

REFERENCES

1. G. P. Sedmale and U. Ya. Sedmalis, "Sintered ceramic materials from hydromica clays," *Steklo Keram.*, No. 1, 25 – 27 (2000).
2. A. D. Shil'tsina and V. I. Vereshchagin, "Ceramic tiles using diopside and argillaceous materials from Khakassia," *Steklo Keram.*, No. 3, 13 – 16 (2000).
3. A. Winchell and H. Winchell, *The Microscopical Characters of Artificial Inorganic Solid Substances: Optical Properties of Artificial Minerals*, New-York (1964).